Vapour-phase Raman Spectra of Group IVB Tetrahalides

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Summary The vapour-phase Raman spectra of 12 tetrahalides of Group IVB have been recorded and values for the *Q*-branches of each fundamental are tabulated; the separation of the *OP* and *RS* branch maxima of the $\nu_2(e)$ mode in each case agrees well with that calculated on the basis of the Placzek–Teller theory.

ALTHOUGH the analysis of *PQR* rotational structure of i.r.-active bands is well known, few studies of the related *OPQRS* structure of Raman-active bands have yet been carried out. This arises partly because of the greater difficulty of analysis in the Raman case, where the rotational selection rules are more relaxed than in the i.r., and partly owing to the experimental difficulties associated with obtaining appropriate Raman spectra. We have now obtained the Raman spectra of twelve tetrahalides of Group IVB in sealed Pyrex tubes at 20—275°; the temperature was chosen in each case to be the lowest at which any potential structure could be determined in the band attributed to the very weakly Raman-active fundamental $\nu_3(t_2)$. A Spex 1401 monochromator in conjunction with Coherent Radiation Ar^+ and Kr^+ lasers were employed (4880, 5145, and 6471 excitation lines).

Values for the *Q* branches of each of the four fundamentals, $\nu_1(a_1)$, $\nu_2(e)$, $\nu_3(t_2)$, and $\nu_4(t_2)$ are listed in the Table. In

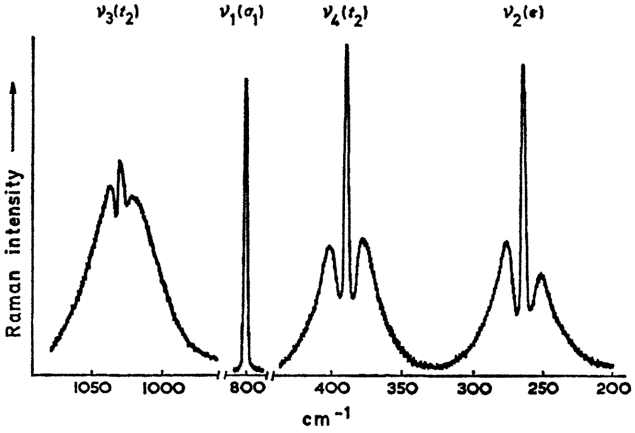

FIGURE. *Vapour-phase Raman spectrum of silicon tetrafluoride at* 22°. *Instrument settings: scanning speed* 10 *cm*$^{-1}$*/min; for* ν_3, *gain* 200 *counts/s, time constant* 2 *s, slits* 100/200/100 *microns, slit height* 10 *mm; for* ν_1, *gain* 500 *counts/s, time constant* 1 *s, slits* 18/200/18 *microns, slit height* 5 *mm; for* ν_4 *and* ν_2, *gain* 200 *counts/s, time constant* 1 *s, slits* 30/200/30 *microns, slit height* 10 *mm.*

accord with the selection rules for spherical top molecules, the $\nu_1(a_1)$ fundamental consists of solely a Q branch in each case. However, the $\nu_2(e)$, $\nu_3(t_2)$ and $\nu_4(t_2)$ fundamentals are all expected to show $OPQRS$ structure. For heavy spherical top molecules of the type under discussion (for which $B < 0{\cdot}2$ cm^{-1}) it is not expected with the present apparatus that the rotational structure will be resolved, nor indeed is it expected for the $\nu_2(e)$ mode of any spherical top molecule that the O branch will be resolved from the P branch or the R branch from the S branch.[2] Thus the central Q branch of this fundamental is expected, and is found, to have a single O,P branch maximum on its low-frequency side, and a single R,S branch maximum on its high-frequency side *e.g.* see Figure. The separation of the branch maxima, $\Delta\nu_{OP,RS}$, is included in each case in the Table. Focussing attention on the $\nu_2(e)$ fundamental (for which no first-order Coriolis effects are operative) the $\Delta\nu_{OP,RS}$ values for each tetrahalide are found to be in close agreement with the values calculated on the basis of the theory of Placzek and Teller,[2] on the basis of which J is considered to be a continuous function. The expressions for the individual branches are, in the case of spherical top molecules, found to be

$$f_P = f_R = f_P^{(0)}(1 + \tfrac{1}{2}x\sqrt{\sigma})$$
$$f_O = f_S = f_O^{(0)}(1 + \tfrac{1}{2}x\sqrt{\sigma})$$

where

$$f_P^{(0)} = \frac{x^2}{10\sqrt{\pi}} \exp\left(-\frac{x^2}{4}\right)$$

$$f_O^{(0)} = \frac{x^2}{80\sqrt{\pi}} \exp\left(-\frac{x^2}{16}\right)$$

$$\sigma = Bhc/kT \qquad B = h/8\pi^2 Ic \text{ (in cm}^{-1}\text{)}$$

and x is the reduced frequency given by

$$x = \Delta\nu_{OP,Q}/(BhckT)^{\frac{1}{2}}$$

Differentiation of the function $f_O + f_P$ with respect to x in order to locate the O,P branch maximum leads to the expression

$$\Delta\nu_{OP,RS} = 2x_{\max}(BkT/hc)^{\frac{1}{2}} \text{ (in cm}^{-1}\text{)}$$

The value of $x_{\max}$ is thus a function of σ, and has been calculated to vary from 2·206 for $\sigma = 0$ to 2·272 for $\sigma = 0{\cdot}01$. The σ-values calculated for each molecule lie within this range. The experimental OP,RS separations (corrected to 20°) lie within 0·4 cm^{-1} of the calculated separations in all cases (see final two columns of the Table).

The separations of the principal branch maxima of the $\nu_3(t_2)$ and $\nu_4(t_2)$ fundamentals of each molecule (referred to loosely in the Table as $\Delta\nu_{OP,RS}$) are very different from those for the corresponding $\nu_2(e)$ fundamental, on account of the first-order Coriolis coupling between ν_3 and ν_4 (the relevant sum rule is $\xi_3 + \xi_4 = \frac{1}{2}$). In fact for $1 > \xi > 0$, the high-frequency wing is a composite of the Q^+, R^-, R^0, R^+, S^-, S^0, and S^+ sub-branches whereas the low-frequency wing is a composite of the Q^-, P^+, P^0, P^-, O^+, O^0, and O^- sub-branches. Detailed analyses of these data yield Coriolis coupling constants[4] by a method which presents some advantages over the more usual one of the analysis of the PQR structure of i.r.-active modes.[5] The main advantage of the Raman method for the present compounds (some of which are very readily hydrolysable) lies in the fact that silica tubing may be used as window material at the relevant scattering frequencies, whereas few window materials are available which permit the recording of the fundamental regions of vapour-phase i.r. spectra of heavy, hydrolysable compounds.

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TABLE

Values for the Q-branches and the $\Delta\nu_{OP,RS}$ branch separations for the fundamentals of each tetrahalide (cm^{-1})

Halide	T°C	$\nu_1(a_1)$	$\nu_2(e)$		$\nu_3(t_2)$		$\nu_4(t_2)$		$\Delta\nu_{OP,RS}$ for ν_2	
		max	max	$\Delta\nu_{OP,RS}$	max	$\Delta\nu_{OP,RS}$	max	$\Delta\nu_{OP,RS}$	Exptl. corrected to 20°	Calc. 20°
CF_4[a]	20	908·4	434·5	27·9	1283·0	26·7	631·2	12·8	27·9	27·9
SiF_4	22	800·8	264·2	23·8	1029·6	14·5	388·7	23·0	23·7	23·6
CCl_4[b]	140	460·0	214·2	17·7	792,765	c	313·5	9·8	14·9	15·1
$SiCl_4$[b]	65	423·1	145·2	14·4	616·5	c	220·3	12·6	13·4	13·2
$GeCl_4$[b]	100	396·1	125·0	14·7	459·0	c	171·0	14·8	13·0	12·6
$SnCl_4$[b]	97	369·1	95·2	13·5	408·2	13·2	126·1	14·0	12·0	11·6
$SiBr_4$	210	246·7	84·8	10·7	494·0	c	133·6	3·1,8·5	8·3	8·3
$GeBr_4$	135	235·7	74·7	9·3	332·0	c	111·1	8·7	7·9	7·8
$SnBr_4$	100	222·1	59·4	8·3	284·0	c	85·9	8·9	7·4	7·3
SiI_4	210	166·3	57·6	7·7	405·0	c	~90	c	6·0	5·8
GeI_4[d]	270	156·0	51·6	8·1	273·0	c	77·3	6·6	6·0	5·6
SnI_4[d]	275	147·7	42·4	7·5	*ca.* 210	c	63·0	7·3	5·5	5·3

[a] The Raman spectrum of CF_4 vapour has been recorded previously, with results in good agreement with those presented here; see B. Monostori and A. Weber, *J. Chem. Phys.*, 1960, **33**, 1867.

[b] The value quoted for the $\nu_1(a_1)$ fundamental of each tetrachloride refers to that of the most abundant isotopic species in each case *i.e.* $M^{35}Cl_3{}^{37}Cl$.

[c] OP and RS branches merge with the Q branch.

[d] Obtained using the 6471 Å excitation line only.

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[1] E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations", McGraw-Hill, New York, 1955.

[2] G. Placzek and E. Teller, *Z. Phys.*, **1933 81,** 209.

[3] The theory was developed for totally symmetric modes, but it appears to apply without change also to doubly degenerate modes in the absence of Coriolis coupling.

[4] F. N. Masri and W. H. Fletcher, *J. Chem. Phys.*, 1970, **52**, 5759; R. J. H. Clark and D. M. Rippon, in preparation.

[5] W. F. Edgell and R. E. Moynihan, *J. Chem. Phys.*, 1957, **27**, 155; the relevant expression is $\Delta\nu_{PR} = 4(BkT/hc)^{\frac{1}{2}}(1 - \xi)$.